**ALKANES**

Molecules containing only hydrogen and carbon atoms are called **hydrocarbons.** Alkanes are a family of hydrocarbons in which C and H atoms are linked by single covalent bonds. Since the C atoms are linked by single covalent bonds, alkanes are **saturated.** Since each C atom is surrounded by 4 other atoms, the shape around each C atom is **tetrahedral** with bond angles of 109.5o.

Structural formulae are only 2 dimensional and show angles of 90o. In three dimensions each bond angle is 109.5o.



e.g. methane

|  |  |  |
| --- | --- | --- |
| **Name** | **Molecular**  **formula** | **Condensed Structural formula** |
| methane | CH4 | CH4 |
| ethane | C2H6 | CH3CH3 |
| propane | C3H8 | CH3CH2CH3 |
| butane | C4H10 | CH3CH2CH2CH3 |
| pentane | C5H12 | CH3CH2CH2CH2CH3 |
| hexane | C6H14 | CH3(CH2)4CH3 |
| heptane | C7H16 | CH3(CH2)5CH3 |
| octane | C8H18 | CH3(CH2)6CH3 |

Alkanes have a general formula.

A hydrocarbon with n carbon atoms would have 2n+2 hydrogen atoms.

Thus the general formula for alkanes is CnH2n+2.

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## Isomerism

## Isomers are molecules that have the same molecular formula (a formula that shows the type and number of atoms in a molecule) but different structural formulae (a formula that shows which atoms are bonded to which and there arrangement in space). There are two types of isomerism.

**Isomerism**

**Structural isomerism**

**Stereo isomerism**

**Structural Isomers** (also called **constitutional isomers**) are molecules that have the same **molecular** formula *but* a different structural formula.

E.g. C5H12

|  |  |  |
| --- | --- | --- |
| Isomer | BP oC | MP oC |
|  | 36.1 | -130 |
|  | 28 | -160 |
|  | 9.5 | -17 |

Because of their different structure, these isomers have different physical properties (m.p., b.p., solubility etc), and may have different chemical properties (particularly if the structural isomers have different functional groups such as CH3COCH3 and CH3CH2CHO).

The molecules shown on page 2 are all called ‘straight chain’ alkanes

e.g. CH3CH2CH2CH2CH3.

Alkanes with 4 or more C atoms can also exist as branched chain molecules.

CH3 - CH2 - CH – CH3

|

CH3

Like pentane, this molecule has molecular formula C5H12 but its structural formula is different and it is a different substance with different melting point, boiling point. It is a **structural isomer** of pentane, since it has the same **molecular** formula but a different **structural** formula.

|  |  |
| --- | --- |
| **Formula** | **Isomers** |
| **C6H14** | **5** |
| **C7H16** | **9** |
| **C8H18** | **18** |
| **C15H32** | **4347** |
| **C20H42** | **366,319** |
| **C30H62** | **4,111,846,763** |

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**Naming alkanes -** Alkanesare named as follows:

1. Identify the longest continuous chain of C atoms.

**CH3-CH2-CH**-CH2-CH3

**hexane**

**|**

**CH2-CH2-CH3**

1. All other C atoms are branches attached to the parent chain and are named according to the number of C atoms in the attached group.
2. In the example above the side chain is shaded and is **ethyl -** note the name ending for the substituent is changed from -ane to -yl.
3. The position of the branch on the parent chain is identified by numbering the carbon atoms from one end of the parent chain. The numbering begins at which ever end gives the lowest possible number. Hence the molecule above is **3-ethylhexane**.

**Note:** The position number is separated from the name by a hyphen. The branch and parent name is all one word.

4. If a molecule has several identical branches, each branch is given a separate number (separated by comas) but the branches are grouped together using the appropriate prefix:

di- 2 identical groups

tri- 3 identical groups.

tetra- 4 identical groups.

*Exercise 1: Draw the structural formulae for each of the following molecules.*

*2,3-dimethylpentane*

*2,2,4-trimethylhexane*

*3-ethyl-2-methylheptane*

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**Physical properties of alkanes**

Alkanes are all colourless. They are all non-polar so they are insoluble in water. They are soluble in each other and are therefore often used as solvents and grease removers. Alkanes are molecular and contain no ions. This means they will not conduct electricity.

The smaller the alkane molecule the lower the boiling point and the more volatile the alkane. As the molar mass increases the boiling points increase as the strength of weak intermolecular forces between molecules increases.

1. The alkanes methane to butane (C1 - C4) are all gases at room temperature.
2. Alkanes with between 5 and about 15 C atoms are all liquids (e.g. kerosene).
3. Alkanes with over 15 atoms are soft solids e.g. candle wax.

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**Reactions of alkanes**

**1. Combustion:** Alkanes readily burn in oxygen, or air, and are commonly used as fuels e.g. LPG, CNG, petrol, kerosene, wax. When they burn they are undergoing combustion and being oxidised. One product is always water. The other product(s) depends on the amount of oxygen present and can be either CO2, CO, or carbon.

a) **Complete combustion -** occurs when the reaction is carried out in excess O2 and the products are CO2 and H2O. Complete combustion produces a hotter, clean burning flame.

CH4 + 2O2 → CO2 + 2H2O

b) **Incomplete combustion -** occurs when the combustion is carried out in a limited supply of air or oxygen. The flame is not clean burning, but is sooty and yellow coloured due to the presence of glowing soot particles, C. The poisonous gas carbon monoxide, CO, can also be produced.

CH4 + 1.5 O2 → CO + 2H2O orCH4 + O2 → C(*s*) + 2H2O

*Exercise 2: Write balanced equations for the complete and incomplete combustion of butane.*

1. **Bromination -**  is the reaction occurring when bromine, Br2, reacts with alkanes. The reaction is very slow and only occurs in the presence of a catalyst such as ultraviolet light (sunlight). The reaction that occurs is a **substitution** in which an H atom is replaced by a Br atom from each Br2 molecule. As the orange bromine molecules are converted to bromoalkane and hydrogen bromide, HBr, (both colourless), the orange colour **slowly** disappears.

sunlight



+ Br2 →

+ H-Br

**Note:** Only one of the Br atoms from each Br2, not both, is substituted!

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**ALKENES AND ALKYNES**

Alkenes and alkynes are both families of **unsaturated** hydrocarbons**.** This isbecause they contain double C=C bonds (alkenes) or triple C≡C bonds (alkynes). Alkenes with one double bond have the general formula CnH2n while alkynes with one triple bond have the general formula CnH2n-2.

To name these molecules, the name ending is simply changed from *-ane­* to *-ene* or *-yne* for alkenes or alkynes respectively. If the carbon chain is more than 3 atoms long, a number will be needed to indicate where the double or triple bond is to be placed.

e.g.



ethene



1-butene OR but-1-ene(number from RHS as this gives lowest number)



2-methylhex-3-ene



propyne

Alkenes can exist as **geometrical** or ***cis-trans* isomers,** a form of stereoisomerism. *Remember, there are two types of isomerism.*

**Isomerism**

**Structural isomerism**

**Stereo isomerism**

**Stereo Isomers** are molecules that have the same **molecular** and **structural** formula but the atoms are arranged differently in space.

A simple example is but-2-ene.



*cis* - but-2-ene *trans* -but-2-ene

These are **geometric isomers.**

To exist as geometrical isomers the C atoms at both ends of the double bond must each have **two different groups (or atoms) attached**.

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**Reactions**

The reactions of unsaturated hydrocarbons can be classed as either

* **combustion** (an oxidation reaction) as for alkanes
* **addition** - a molecule is added across the multiple bond.

Addition results in the formation of a single product from two reactants.

Examples of addition reactions with propene are:

1. Addition of hydrogen gas, H2, which only occurs in the presence of a catalyst (Ni or Pt) at high temperatures.

Pt



+ H2 🡺

1. Addition of halogens, Br2 and Cl2, to form dibromo or dichloroalkanes



+ Br2 →

1,2-dibromopropane

This reaction is **rapid** and does not require a catalyst such as sunlight. Addition of an alkene to bromine results in the rapid decolourisation of the orange bromine i.e. it goes from orange to **colourless**.This is commonly used as a test for the presence of unsaturation.

(iii) Asymmetric molecules such as HCl and H2O can also be added to alkanes resulting in the formation of **two** possible products. e.g. as propene is an asymmetric hydrocarbon, the two possible products are:



+ HBr →

OR 1-bromopropane



+ HBr →

2-bromopropane

The **major** product is the one in which the H atom of HBr attaches to the C atom with the **most H atoms** already (Markovnikov’s rule).

This is called the “rich get richer” rule. This means that in the reaction above the major product will be 2-bromopropane.

(iv) Addition of water, H2O, in the form of steam at a high temperature and pressure in the presence of an acid catalyst, also results in a major and minor product being possible.



+ H2O →

propan-2-ol (**major** product)

**or**



+ H2O →

propan-1-ol (**minor** product)

(v) Addition polymerisation - This is the formation of a long chain molecule by a large number of alkene molecules adding together at their double bonds. If the starting alkene, the monomer, is ethene the polymer formed is called polyethene or polythene.

**Note:** The polymer is fully saturated and has no double bonds.



+ + +

forms

- polythene. or -(CH2CH2)-n



If the monomer is vinylchloride (or chloroethene) the polymer is polyvinyl chloride, PVC, where every **second** carbon atom has a chlorine atom attached to it.

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**Test for alkenes using aqueous potassium permanganate**

Another important reaction of unsaturated hydrocarbons is their reaction with dilute aqueous solutions of purple potassium permanganate, KMnO4. The alkene is converted to a diol in this reaction.

KMnO4



→

propane-1,2-diol

The colour change which is observed depends on whether the reaction is carried out in acidic or neutral conditions:

1. In neutral aqueous KMnO4 the purple colour of the permanganate ion disappears as it is reduced and a brown solid, MnO2, forms.
2. In acidic KMnO4 the purple solution is decolourised forming the colourless Mn2+ ion.

**Preparation of ethene.**

1. The dehydration of ethanol, CH3CH2OH, by heating it with a dehydrating agent such as conc sulfuric acid.

conc H2SO4

CH3CH2OH → CH2 = CH2 + H2O

heat

**Preparation of ethyne**

In the laboratory ethyne is prepared by the reaction of water with calcium carbide.

CaC2 + 2H2O → C2H2(*g*) + Ca(OH)2

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# ALCOHOLS

Alcohols are a homologous series of molecules that have the -O-H functional group. They can be represented as ROH where R is an alkyl group. They are named as for alkanes but with the final -e replaced by **ol.**

CH3OH methanol



CH3CH2OH ethanol



CH3CH2 CH2OH propan-1-ol

CH3CHOHCH3 propan-2-ol



Alcohols (and chloroalkanes) are classified as primary, secondary or tertiary, depending on the number of C atoms that are directly attached to the C atom carrying the OH group (or Cl).

i.e.

primary RCH2OH,

secondary R2CHOH,

tertiary R3COH.

*Exercise*

*1. Name and label each of the following alcohols as primary, secondary or tertiary.*



CH3CH2OH

*2. Draw structural formulae for and classify each of the following alcohols:*

*a) butan-2-ol*

*b) 3-methylpentan-1-ol*

*c) 2-methylhexan-2-ol*

**Preparation**

1. **Methanol** is prepared from natural gas, which contains CH4. This is done at the Motonui synthetic petrol plant in Taranaki.

**b) Ethanol** is produced by

i) anaerobic (without oxygen) fermentation of sugars in grapes, etc. The enzymes in yeast (the catalyst) convert glucose to ethanol and CO2. This is the method of producing ethanol for drinking in wine, beer etc.

yeast

C6H12O6 → 2CO2(*g*) + 2CH3CH2OH

ii) hydration of ethene using a catalyst as well as high temperature and pressure. This is the method of producing industrial ethanol.

CH2 = CH2(*g*) + H2O(*g*) →

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Properties:

The smallest alcohols are all liquids that are soluble in water (because of the polar O-H bond). As the non-polar alkyl chain increases in length the molecules become more non-polar and more insoluble in water. Like the hydrocarbons, the melting and boiling points increase with molar mass.

# Reactions of alcohols

Alcohols react in 4 important ways:

1. **combustion -** used as a fuel alcohols, especially methanol and ethanol are clean burning in air and produce CO2(g) and H2O(g) - provided there is sufficient oxygen present.

CH3CH2OH(*g*) + 3O2 🡺 2CO2 + 3H2O

1. **oxidation –** primary alcohols can be oxidised to form carboxylic acids.

Cr2O72− /H+

CH3CH2OH(*g*) 🡺 CH3CO2H

The orange colour (colour of dichromate ion Cr2O72−), changes to green (colour of Cr3+). This is the reaction observed in a positive test using the old breathalyser.

When KMnO4 is used to oxidise primary alcohols the colour change is from purple to colourless.

**NOTE:** Oxidation of alcohols can also lead to families of compounds called aldehydes and ketones

1. **Dehydration** (elimination) produces alkenes by removal of water. This is done by heating with conc sulfuric acid, a dehydrating agent.

conc H2SO4

CH3CH2OH → CH2 = CH2 + H2O

Heat

1. Reaction of alcohols with carboxylic acids results in the formation of **esters,** an esterification reaction.

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# CARBOXYLIC ACIDS

This is a homologous series of molecules containing the



functional group - COOH, or written structurally as

When naming carboxylic acids it is important to include the C atom of the COOH group when finding the parent name. The systematic name is the parent alkane with the -e removed and replaced by -oic acid.

CH3COOH or CH3CO2H ethanoic acid

(acetic acid)

HCOOH or HCO2H methanoic acid

(formic acid)

**Properties**

Short chain carboxylic acids are soluble in water because the COOH group is polar. As the alkyl chain increases in length the acids become increasingly non-polar and less soluble in water. Long chain carboxylic acids are commonly called ‘fatty acids’ because of their insolubility.

Carboxylic acids are weak acids and only slightly dissociate in water to form the hydronium ion, H3O+, and the alkanoate ion.

CH3COOH(*aq*) + H2O



CH3COO−(*aq*)  + H3O+(*aq*)

Aqueous solutions of carboxylic acids have the following properties.

* They turn blue litmus pink.
* They react with some metals forming hydrogen gas

The reaction equation can be written as follows:

2CH3COOH(*aq*) + Mg(*s*) →

2CH3COO−(*aq*) + Mg2+(*aq*) + H2(*g*)

* Carboxylic acids react with metal carbonates giving off CO2 gas.
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**ESTERS**

Carboxylic acids react with alcohols, in the presence of conc sulfuric acid as a catalyst, to form **esters**.

When ethanoic acid is reacted with methanol the ester, methyl ethanoate is formed.



H3O+ + CH3OH



heat

+ H2O

Esters are a family of organic compounds that contain the ester H2O functional group where R and R1 are alkyl groups (or R is hydrogen if methanoic acid was used in the preparation).



Many esters occur naturally and can often be identified by their fruity odour.

*Exercise:*

*1) Write equations using structural formulae for the formation of the following esters*

*a) ethyl methanoate from ethanol and methanoic acid*

*b) butyl propanoate from butan-1-ol and propanoic acid*

*2) Name the ester that would be formed by reacting*

*a) propan-1-ol and ethanoic acid*

*b) butanoic acid and methanol*

*3) Draw the structural formulae for the esters formed in Ex 2 above.*

*4) Name the alcohol and carboxylic acid that would react together to form*

1. *ethyl pentanoate*
2. *butyl octanoate*

**Hydrolysis of esters**

The hydrolysis of an ester in aqueous solution results in the break up of the ester and the formation of an alcohol and the carboxylic acid or carboxylate ion (depending on the pH of the solution).

1. Hydrolysis in acid produces the alcohol + carboxylic acid.

CH3CH2COOCH3 + H2O / H+ →

CH3CH2COOH + CH3OH

methyl propanoate

propanoic acid methanol

1. Hydrolysis in NaOH soln gives alcohol + the **sodium salt** of the carboxylic acid.

CH3CH2COOCH3 + NaOH →

CH3CH2COO−Na+ + CH3OH

sodium propanoate

**Fats and oils**

Fats and oils (lipids) are all triesters made from glycerol (propane-1,2,3-triol) and three long chain carboxylic acids (fatty acids) as shown below. The ester link forms between the -OH group of the alcohol and the -H atom from the carboxylic acid with the elimination of water. Glycerol is an example of a”triol” which has three -OH groups present. Each of these can form an ester link with a **different** carboxylic acid, for example the fat called stearin.



+ R1COOH

+ R2COOH →

+ R3COOH

+ 3H2O

# Soap

The three ester links present in these molecules can be broken (or hydrolysed) by heating with sodium hydroxide solution. This releases the glycerol molecule plus the sodium salts of the long chain fatty acids which are soaps. This “saponification” process is shown in the diagram below.



+ 3NaOH →

+ 3R3COO−Na+

Soaps work because the tail of the molecule is a long non-polar hydrocarbon chain (from the fatty acid) which readily dissolves grease and dirt (as “like dissolves like”). Then the ionic carboxylate ion readily dissolves in water (which is also polar) and is able to carry away the grease with it in the rinse water.



non-polar hydrocarbon tail (dissolves grease)

polar carboxylate head (dissolves in water)